CLAIMS

1. A crosslinked polymer obtainable by radical polymerisation of ethylenically unsaturated monomers including

a) a zwitterionic monomer of the general formula I

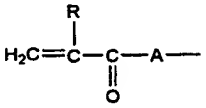
YBX I

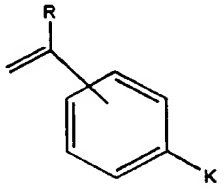
wherein

B is a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene chain optionally containing one or more fluorine atoms up to and including perfluorinated chains or, if X or Y contains a terminal carbon atom bonded to B, a valence bond;

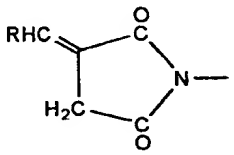
X is a zwitterionic group; and

Y is an ethylenically unsaturated polymerisable group selected from

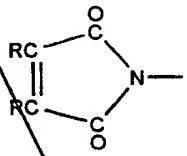




$CH_2=C(R)-CH_2-O-$, $CH_2=C(R)-CH_2OC(O)-$, $CH_2=C(R)OC(O)-$, $CH_2=C(R)-O-$, $CH_2=C(R)CH_2OC(O)N(R^1)-$, $R^2OOCCR=CRC(O)-O-$, $RCH=CHC(O)O-$, $RCH=C(COOR^2)CH_2-C(O)-O-$,



and



wherein:

R is hydrogen or a C_1-C_4 alkyl group;

R^1 is hydrogen or a C_1-C_4 alkyl group or R^1 is -B-X where B and X are as defined above; and

R^2 is hydrogen or a C_{1-4} alkyl group or BX where B and X are as defined above;

A is -O- or $-NR^1-$;

K is a group $-(CH_2)_pOC(O)-$, $-(CH_2)_pC(O)O-$,

$-(CH_2)_pOC(O)O-$, $-(CH_2)_pNR^3-$, $-(CH_2)_pNR^3C(O)-$,

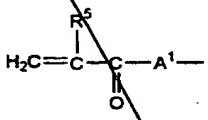
$-(CH_2)_pC(O)NR^3-$, $-(CH_2)_pNR^3C(O)O-$, $-(CH_2)_pOC(O)NR^3-$,

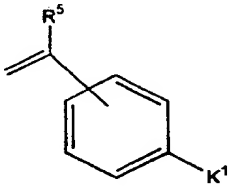
$-(CH_2)_pNR^3C(O)NR^3-$ (in which the groups R^3 are the same or different), $-(CH_2)_pO-$, $-(CH_2)_pSO_3-$, or, optionally in combination with B, a valence bond and p is from 1 to 12 and R^3 is hydrogen or a C_1-C_4 alkyl group.

b) an aromatic group containing monomer of the general formula II

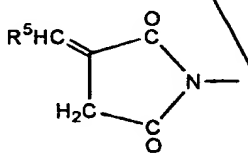
$$Y^1R^4 \qquad II$$

wherein Y^1 is selected from

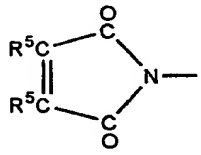




$CH_2=C(R^5)-CH_2-O-$, $CH_2=C(R^5)-CH_2\ OC(O)-$, $CH_2=C(R^5)OC(O)-$, $CH_2=C(R^5)-O-$, $CH_2=C(R^5)CH_2OC(O)N(R^6)-$, $R^7OOCCR^5=CR^5C(O)-O-$, $R^5CH=CHC(O)O-$, $R^5CH=C(COOR^7)CH_2-C(O)-O-$,



and



wherein:

R^5 is hydrogen or a C_1-C_4 alkyl group;

R^6 is hydrogen or a C_1-C_4 alkyl group or R^5 is R^3; and

R^7 is hydrogen or a C_{1-4} alkyl group or R^3

A^1 is -O- or $-NR^6-$;

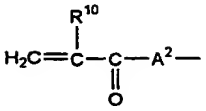
K^1 is a group $-(CH_2)_qOC(O)-$, $-(CH_2)_qC(O)O-$, $-(CH_2)_qOC(O)O-$, $-(CH_2)_qNR^8-$, $-(CH_2)_qNR^8C(O)-$, $-(CH_2)_qC(O)NR^8-$, $-(CH_2)_qNR^8C(O)O-$, $-(CH_2)_qOC(O)NR^8-$, $-(CH_2)_qNR^8C(O)NR^8-$ (in which the groups R^8 are the same or different), $-(CH_2)_qO-$, $-(CH_2)_qSO_3-$, or a valence bond and p is from 1 to 12 and R^8 is hydrogen or a C_1-C_4 alkyl group;

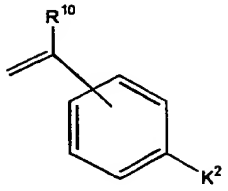
and R^4 is an aromatic group; and

c) a cross-linking monomer of the general formula III

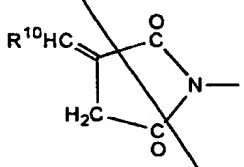
$$(Y^2)_nR^9 \qquad III$$

in which n is an integer of at least 2, each Y^2 is selected from





$CH_2=C(R^{10})-CH_2-O-$, $CH_2=C(R^{10})-CH_2\,OC(O)-$, $CH_2=C(R^{10})OC(O)-$, $CH_2=C(R^{10})-O-$, $CH_2=C(R^{10})CH_2OC(O)N(R^{11})-$, $R^{12}OOCCR^{10}=CR^{10}C(O)-O-$, $R^{10}CH=CHC(O)O-$, $R^{10}CH=C(COOR^{12})CH_2-C(O)-O-$,



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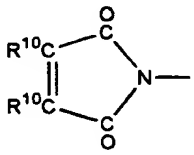


wherein:

R^{10} is hydrogen or a C_1-C_4 alkyl group;

R^{11} is hydrogen or a C_1-C_4 alkyl group or R^{11} is R^4; and

R^{12} is hydrogen or a C_{1-4} alkyl group or R^3

A^2 is -O- or $-NR^{11}$-;

K^2 is a group $-(CH_2)_rOC(O)-$, $-(CH_2)_rC(O)O-$, $-(CH_2)_rOC(O)O-$, $-(CH_2)_rNR^{12}-$, $-(CH_2)_rNR^{12}C(O)-$, $-(CH_2)_rC(O)NR^{12}-$, $-(CH_2)_rNR^{12}C(O)O-$, $-(CH_2)_rOC(O)NR^{12}-$, $-(CH_2)_rNR^{12}C(O)NR^{12}-$ (in which the groups R^{12} are the same or different), $-(CH_2)_rO-$, $-(CH_2)_rSO_3-$ or a valence bond and r is from 1 to 12 and R^{12} is hydrogen or a C_1-C_4 alkyl group;

and R^9 is an n-functional organic group.

2. A polymer according to claim 1 in which R^4 is benzyl or phenyl.

3. A polymer according to any preceding claim in which Y and Y^2 are the same, and are preferably $CH_2=CR^xCOA$, in which R^x is R and R^{10} and is methyl or hydrogen and A is O.

4. A polymer according to any preceding claim in which R^9 is an aromatic group preferably a bis-phenol A group.

5. A polymer according to any preceding claim which includes a crosslinking agent in which R^9 is an aliphatic group, preferably an ethylene or an oligo(ethyleneoxy)ethylene group.

6. A polymer according to any of claims 1 to 3 in which the monomers include a mixture of at least two cross-linking monomers of the general formula III, in at least one of which R^9 is an aromatic group, preferably a bisphenol A group, and at least one of which R^9 is an aliphatic group, preferably an ethylene or oligo (ethyleneoxy)ethylene group.

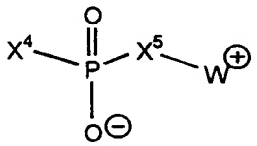
7. A polymer according to claim 6 in which the molar ratio of crosslinking monomer in which R^9 is aromatic to crosslinking monomer in which R^9 is aliphatic is in the range 10:1 to 1:10, preferably 5:1 to 1:5, most preferably 2:1 to 1:2.

8. A polymer according to any preceding claim in which the zwitterionic monomer is present in molar amount in the range 1 to 95%, preferably 5 to 50%, more preferably 10 to 25%, based on total ethylenically unsaturated monomer.

9. A polymer according to any preceding claim in which the aromatic group containing monomer is present in a molar amount in the range 10 to 99%, preferably 50 to 95%, more preferably 75 to 90%, based on total ethylenically unsaturated monomer.

10. A polymer according to any preceding claim in which the crosslinking monomer is present in a molar amount in the range 0.01 to 10%, preferably 0.1 to 5%, more preferably in the range 0.5 to 3% based on total ethylenically unsaturated monomer.

11. A polymer according to any preceding claim in which the zwitterionic group has the general formula IV



IV

in which the moieties X^4 and X^5, which are the same or different, are -O-, -S-, -NH- or a valence bond, preferably -O-, and W^+ is a group comprising an ammonium, phosphonium or sulphonium cationic group and a group linking the anionic and cationic moieties which is preferably a C_{1-12}-alkylene group,

preferably in which W^+ is a group of formula

$-W^1-N^+R^{14}_3$, $-W^1-P^+R^{15}_3$, $-W^1-S^+R^{15}_2$ or $-W^1$-Het$^+$ in which:

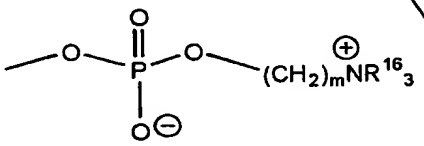
W^1 is alkylene of 1 or more, preferably 2-6 carbon atoms optionally containing one or more ethylenically unsaturated double or triple bonds, disubstituted-aryl, alkylene aryl, aryl alkylene, or alkylene aryl alkylene, disubstituted cycloalkyl, alkylene cycloalkyl, cycloalkyl alkylene or alkylene cycloalkyl alkylene, which group W^1 optionally contains one or more fluorine substituents and/or one or more functional groups; and

either the groups R^{14} are the same or different and each is hydrogen or alkyl of 1 to 4 carbon atoms, preferably methyl, or aryl, such as phenyl or two of the groups R^{14} together with the nitrogen atom to which they are attached form a heterocyclic ring containing from 5 to 7 atoms or the three groups R^{14} together with the nitrogen atom to which they are attached form a fused ring structure containing from 5 to 7 atoms in each ring, and optionally one or more of the groups R^{14} is substituted by a hydrophilic functional group, and

the groups R^{15} are the same or different and each is R^{14} or a group OR^{14}, where R^{14} is as defined above; or

Het is an aromatic nitrogen-, phosphorus- or sulphur-, preferably nitrogen-, containing ring, for example pyridine,

12. A polymer according to claim 11 in which X is a group of formula V:



V

where the groups R^{16} are the same or different and each is hydrogen or C_{1-4} alkyl, and

m is from 1 to 4,

in which preferably the groups R^{16} are the same.

13. A gel comprising a polymer according to any preceding claim swollen by a liquid.

14. A gel according to claim 13 in which the liquid is aqueous.

15. A refractive device formed of a polymer according to any of claims 1 to 12.

16. A device according to claim 15 which has an average transmission for visible light in the range 400 to 700nm wavelength of at least 90% (when swollen by water).

17. A device according to claim 15 or claim 16 which comprises an absorber of electromagnetic radiation, preferably of U.V. light.

18. A device according to any of claims 15 to 17, having a refractive index when fully swollen in water in the range 1.45-1.60.

19. A polymerisation process in which a polymerisation mixture containing ethylenically unsaturated monomers is subjected to radical polymerisation, whereby addition polymerisation of the ethylenically unsaturated groups takes place, and in which the monomers include

a) a zwitterionic monomer of the general formula I

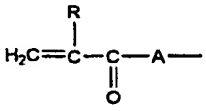
YBX I

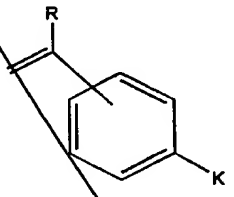
wherein

B is a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene chain optionally containing one or more fluorine atoms up to and including perfluorinated chains or, if X or Y contains a terminal carbon atom bonded to B, a valence bond;

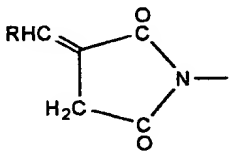
X is a zwitterionic group; and

Y is an ethylenically unsaturated polymerisable group selected from

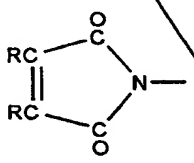




$CH_2=C(R)-CH_2-O-$, $CH_2=C(R)-CH_2\ OC(O)-$, $CH_2=C(R)OC(O)-$, $CH_2=C(R)-O-$, $CH_2=C(R)CH_2OC(O)N(R^1)-$, $R^2OOCCR=CRC(O)-O-$, $RCH=CHC(O)O-$, $RCH=C(COOR^2)CH_2-C(O)-O-$,



and



wherein:

R is hydrogen or a C_1-C_4 alkyl group;

R^1 is hydrogen or a C_1-C_4 alkyl group or R^1 is -B-X where B and X are as defined above; and

R^2 is hydrogen or a C_{1-4} alkyl group or BX where B and X are as defined above;

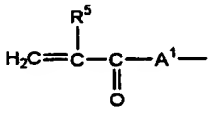
A is -O- or -NR^1-;

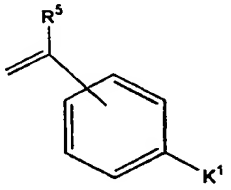
K is a group -$(CH_2)_pOC(O)$-, -$(CH_2)_pC(O)O$-, -$(CH_2)_pOC(O)O$-, -$(CH_2)_pNR^3$-, -$(CH_2)_pNR^3C(O)$-, -$(CH_2)_pC(O)NR^3$-, -$(CH_2)_pNR^3C(O)O$-, -$(CH_2)_pOC(O)NR^3$-, -$(CH_2)_pNR^3C(O)NR^3$- (in which the groups R^3 are the same or different), -$(CH_2)_pO$-, -$(CH_2)_pSO_3$-, or, optionally in combination with B, a valence bond and p is from 1 to 12 and R^3 is hydrogen or a C_1-C_4 alkyl group.

b) an aromatic group containing monomer of the general formula II

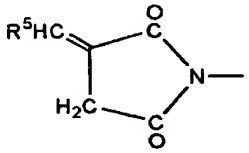
$$Y^1R^4 \qquad \text{II}$$

wherein Y^1 is selected from

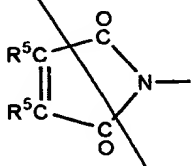




$CH_2=C(R^5)$-CH_2-O-, $CH_2=C(R^5)$-CH_2 OC(O)-, $CH_2=C(R^5)OC(O)$-, $CH_2=C(R^4)$-O-, $CH_2=C(R^5)CH_2OC(O)N(R^6)$-, $R^7OOCCR^5=CR^5C(O)$-O-, $R^5CH=CHC(O)O$-, $R^5CH=C(COOR^7)CH_2$-C(O)-O-,



and



wherein:

R^5 is hydrogen or a C_1-C_4 alkyl group;

R^6 is hydrogen or a C_1-C_4 alkyl group or R^6 is R^4; and

R^7 is hydrogen or a C_{1-4} alkyl group or R^4

A^1 is -O- or -NR^6-;

K^1 is a group -$(CH_2)_qOC(O)$-, -$(CH_2)_qC(O)O$-, -$(CH_2)_qOC(O)O$-, -$(CH_2)_qNR^8$-, -$(CH_2)_qNR^8C(O)$-, -$(CH_2)_qC(O)NR^8$-, -$(CH_2)_qNR^8C(O)O$-, -$(CH_2)_qOC(O)NR^8$-,

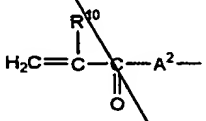
$-(CH_2)_qNR^8C(O)NR^8-$ (in which the groups R^8 are the same or different), $-(CH_2)_qO-$, $-(CH_2)_qSO_3-$, or a valence bond and p is from 1 to 12 and R^8 is hydrogen or a C_1-C_4 alkyl group,

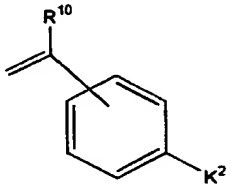
and R^4 is an aromatic group; and

c) a cross-linking monomer of the general formula III

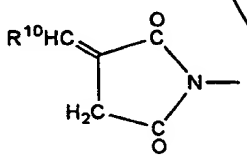
$$(Y^2)_nR^9 \qquad \text{III}$$

in which n is an integer of at least 2, each Y^2 is selected from





$CH_2=C(R^{10})$-CH_2-O-, $CH_2=C(R^{10})$-CH_2 OC(O)-, $CH_2=C(R^{10})OC(O)$-, $CH_2=C(R^{10})$-O-, $CH_2=C(R^{10})CH_2OC(O)N(R^{11})$-, $R^{12}OOCCR^{10}=CR^{10}C(O)$-O-, $R^{10}CH=CHC(O)O$-, $R^{10}CH=C(COOR^{12})CH_2$-C(O)-O-,



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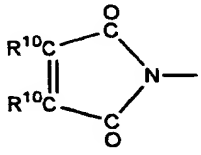

wherein:

R^{10} is hydrogen or a C_1-C_4 alkyl group;

R^{11} is hydrogen or a C_1-C_4 alkyl group or R^{11} is R^4; and

R^{11} is hydrogen or a C_{1-4} alkyl group or R^3;

A^2 is -O- or $-NR^{11}$-;

K^2 is a group $-(CH_2)_rOC(O)$-, $-(CH_2)_rC(O)O$-, $-(CH_2)_rOC(O)O$-, $-(CH_2)_rNR^{12}$-, $-(CH_2)_rNR^{12}C(O)$-, $-(CH_2)_rC(O)NR^{12}$-, $-(CH_2)_rNR^{12}C(O)O$-, $-(CH_2)_rOC(O)NR^{12}$-, $-(CH_2)_rNR^{12}C(O)NR^{12}$- (in which the groups R^{12} are the same or different), $-(CH_2)_rO$-, $-(CH_2)_rSO_3$- or a valence bond and r is from 1 to 12 and R^{12} is hydrogen or a C_1-C_4 alkyl group;

and R^9 is an n-functional organic group.

20. A process according to claim 19 in which the zwitterionic monomer is present in molar amount in the range 1 to 95%, preferably 5 to 50%, more preferably 10 to 25%, based on total ethylenically unsaturated monomer.

21. A process according to claim 19 or claim 20 in which the aromatic group containing monomer is present in a molar amount in the range 10 to 99%, preferably 50 to 95%, more preferably 75 to 90%, based on total ethylenically unsaturated monomer.

22. A process according to any of claims 19 to 21 in which the crosslinking monomer is present in a molar amount in the range 0.01 to 10%, preferably 0.1 to 5%, more preferably in the range 0.5 to 3% based on total ethylenically unsaturated monomer.

23. A process according to any of claims 19 to 22 in which polymerisation is initiated by a thermal, a redox or a U.V. initiator.

24. A process according to any of claims 19 to 23 in which the zwitterionic monomer and aromatic group containing monomer are immiscible in the absence of a co-solvent, and in which the polymerisation mixture contains a co-solvent which is a non-polymerisable liquid whereby the polymerisation mixture is a homogeneous solution.

25. A process according to claim 24 in which the co-solvent is an alcohol.

26. A process according to claim 24 or claim 25 in which the co-solvent is present in the polymerisation mixture in an amount in the range 5 to 90% by weight, preferably in the range 10 to 75%, more preferably 10 to 50% by weight.

27. A process of forming a refractive device in which a polymerisation process according to any of claims 24 to 26 is carried out, the co-solvent is removed from the product polymer and the xerogel which is substantially free of co-solvent is shaped by cutting to a predetermined three dimensional shape.

28. A process according to claim 27 in which the product is used as an intraocular lens.

29. A process of forming a refractive device in which a polymerisation process according to any of claims 24 to 26 is carried out whilst the polymerisation mixture is in a mould and, after polymerisation, the solvent is removed from the polymer, usually after removal from the mould, preferably by replacement with a second solvent.

30. A process according to any of claims 27 to 29 in which polymer product is water-swellable and the shaped or moulded product is swollen in aqueous liquid.

31. A process according to any of claims 19 to 30 having the further features defined in any of claims 2 to 7, 11 and 12.

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